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STRUCTURE OF MOLECULAR ADSORBATES ON SURFACES(U)
PITTSBURGH UNIV PA SURFACE SCIENCE CENTER J T VATES
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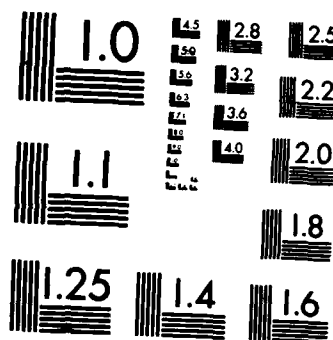
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2. **PRINCIPAL INVESTIGATOR:** John T. Yates, Jr.
 Department of Chemistry
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6. **SENIOR RESEARCH PERSONNEL:** Dr. Craig Klauber
 Dr. Miles Dresser
 Dr. Anne-Marie Lanzillotto

7. **JUNIOR RESEARCH PERSONNEL:** Mr. Mark Alvey
 Mr. Kurt Kolasinski

8. **PUBLICATIONS:**

1. "Evidence for Chemisorption Site Selection Based on an Electron Donor Mechanism," C. Klauber, M. D. Alvey, J. T. Yates, Jr., Chem. Phys. Letters 106, 477 (1984).
2. "NH₃ Adsorption on Ni(110) and the Production of the NH₂ Species by Electron Irradiation," C. Klauber, M. D. Alvey and J. T. Yates, Jr., Surface Science 154, 139 (1985).
3. "Summary Abstract: "Surface Bonding of the NH₃ and NH₂ Species to Ni(110)," M. D. Alvey, C. Klauber and J. T. Yates, Jr., J. Vac. Sci. & Technol A 3(3), 1631 (1985).
4. "ESDIAD Studies of the Structure of Species Chemisorbed on Ni(110). The Surface Bonding of NH₃, NH₂ and CO," J. T. Yates, Jr., C. Klauber and M. D. Alvey, Proceedings of Second International Workshop, Desorption Induced by Electronic Transitions DIET-II, Schloss Elmau, Bavaria, October 15-17, 1984; Eds. W. Brenig and D. Menzel, Springer-Verlag, Berlin, 1985.
5. "A Coverage-Induced Tilting of CO Molecules Adsorbed on Ni(110)," J. Lee, H. Metiu, R. M. Martin, J. Arias, C. Hanrahan, C. Klauber, M. D. Alvey, and J. T. Yates, Jr., Surface Science, 159, L460 (1985).



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PUBLICATIONS (continued)

6. "Metastable Angular Distributions from Electron Stimulated Desorption," Mark D. Alvey, Miles J. Dresser, and J. T. Yates, Jr., Phys. Rev. Lett. 56(4), 367 (1986).
7. "Conformational Changes in Chemisorbed CO on Ni(110) Due to Molecular Interactions: An ESDIAD Study," Mark D. Alvey, Miles J. Dresser, and J. T. Yates, Jr., Surface Science 165, 447 (1986).
8. "Enhancement of the ESDIAD Method for Imaging Bond Directionality in Chemisorbed Species," M. J. Dresser, M. D. Alvey, and J. T. Yates, Jr., Surface Science, 169, 91 (1986).
9. "An Enhanced ESDIAD Method for Imaging Molecular Orientations of Adsorbed Species," M. J. Dresser, M. D. Alvey, and J. T. Yates, Jr., J. Vac. Sci. & Technol., A 4(3), 1446 (1986).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

—This project had as its primary objective the extension of the ESDIAD (electron stimulated desorption ion angular distribution) method to the study of interesting molecular adsorbates structure on single crystal surfaces. A second objective was to develop a digital ESDIAD apparatus capable of more accurate study of ion angular distributions from the ESDIAD phenomena. The fundamental fact that positive ions are ejected from adsorbates along the fragmentation bond direction was employed in all of these studies. The following basic facts were determined in the 9 papers published on this contract.

- a. NH_3 , an electron donor molecule, seeks the electropositive Ni bonding sites on the corrugated Ni(110) crystal.
- b. The NH_3 molecule is not subject to axial rotational barriers greater than about 8 meV on these sites, i.e., the molecule shows no preferential N-H bonding azimuth, and seems to rotate freely above 30 K.
- c. $\text{NH}_3(\text{a})$ can be quantitatively converted to $\text{NH}_2(\text{a})$ by electron bombardment with a cross section of 1.6 \AA^2 for 55 eV electrons.
- d. The $\text{NH}_2(\text{a})$ species is locked to the Ni(110) lattice with its plane in the (001) and (00 $\bar{1}$) directions.

Cont'd

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS (Continued)

- e. $\text{NH}_2(\text{a})$ thermally decomposes, forming $\text{N}(\text{a}) + \text{H}(\text{a})$ at about 375 K. $\text{NH}_3(\text{a})$ does not thermally decompose, but desorbs as the intact species.
- f. CO chemisorbs on atop Ni sites on Ni(110) forming a vertical C-O bond for coverages below 0.75 CO/Ni. Above this coverage, CO...CO repulsions cause the C-O bond axis to tip, alternately left and right by $\pm 19^\circ$. This transition corresponds to the production of a crowded p1g1 LEED structure.
- g. Metastable Quenching Spectroscopy, involving He^* probe atoms, confirms the result in statement f above, and the tilting results in increased exposure of the 2π orbital to the incoming He^* atoms.
- h. The digital ESDIAD apparatus may be employed for accurate analysis of ion trajectories. A troublesome X-ray background effect, present in all ESDIAD measurements heretofore, can be eliminated using the digital method.
- i. The digital ESDIAD apparatus has been used to make the first angular distribution measurements of electronically excited neutral species produced by electron bombardment. It was found that CO^* (a 3π likely) is sharply-peaked in its emission direction like the positive ions in ESD.

Cont'd
The studies listed above, and considered together, have affirmed the utility of digital ESDIAD to deliver information about the detailed orientation of chemical bonds at surfaces, and about the molecular dynamics of surface species on single crystals.

10. INDIVIDUAL ABSTRACTS OF WORK PUBLISHED

- 1. "Evidence for Chemisorption Site Selection Based on an Electron Donor Mechanism"

ABSTRACT

The orientation of NH_3 chemisorbed on the Ni(110) surface indicates that an electron donor type adsorbate will choose electropositive ridge atom sites in preference to available sites of higher coordination within the surface valleys.

2. NH_3 Adsorption on Ni(110) and the Production of the NH_2 Species by Electron Irradiation

ABSTRACT

The adsorption of NH_3 on Ni(110) has been examined using electron stimulated desorption ion angular distribution (ESDIAD), low energy electron diffraction (LEED) and thermal desorption spectrometry (TDS). At ~ 85 K the NH_3 molecule enters into a series of chemisorption and physisorption states whose structures have been partially characterized by means of ESDIAD and LEED. Upon heating, these NH_3 states desorb without dissociation; for adsorption below 300 K there is essentially no thermal decomposition. The ammonia adlayer was found to be extremely sensitive to electron irradiation effects. Evidence was found to support the irradiation induced conversion of $\text{NH}_3(\text{ads})$ to an amido intermediate, $\text{NH}_2(\text{ads})$. The NH_2 adsorbs with its C_{2v} axis normal to the surface and its N-H bonds aligned along the $[001]$ and $[00\bar{1}]$ directions. In the absence of further electron irradiation the $\text{NH}_2(\text{ads})$ species is stable to 375 K whereupon it dissociates to $\text{N}(\text{ads})$ and $\text{H}_2(\text{g})$. The remaining $\text{N}(\text{ads})$ desorbs with significant attractive $\text{N}\cdots\text{N}$ interaction. No evidence is found for an imido intermediate, $\text{NH}(\text{ads})$. $\text{NH}_2(\text{ads})$ also undergoes a disproportionation/recombination reaction upon heating to produce an additional NH_3 desorption state. A significant isotope effect for N-H versus N-D scission, sensitive to the adsorption state of the ammonia, is found to occur upon electron irradiation.

3. "Summary Abstract: Surface Bonding of the NH_3 and NH_2 Species to Ni(110)"

ABSTRACT

Using electron impact, we have converted $\text{NH}_3(\text{ads})$ on the Ni(110) surface. Below 300 K, NH_3 is bound nondissociatively to Ni ridge atoms on Ni(110) by electron donation from lone pair N electrons. Upon electron bombardment, the process $\text{NH}_3(\text{ads}) \xrightarrow{e^-(55 \text{ eV})} \text{NH}_2(\text{ads}) + \text{H}(\text{ads})$ occurs quantitatively with a cross section of 1.6 \AA^2 . ESDIAD results indicate that the initial NH_3 species is oriented normally to the (110) surface with no azimuthal ordering down to 29 K. In contrast, NH_2 is azimuthally ordered at 300 K with the plane of the species perpendicular to the rows of Ni atoms on the surface; this bonding orientation is consistent with the molecular orbital structure of NH_2 . This species is stable to 375 K where it decomposes to $\text{N}(\text{ads})$ and $\text{H}_2(\text{g})$.

4. "ESDIAD Studies of the Structure of Species Chemisorbed on Ni(110). The Surface Bonding of NH₃, NH₂ and CO"

ABSTRACT

NH₃ is chemisorbed at 90 K as an undissociated molecular species on Ni(110). Previous reports by others of the thermal dissociation of this molecule on Ni surfaces are probably due to inadvertent electron bombardment which efficiently degrades NH₃(ads) to NH₂(ads). Our results taken together suggest that detailed local structural information about chemisorbed species is able to be obtained through the use of the ESDIAD method. The qualitative observation of the symmetry of ESD-generated positive ion fragments from chemisorbed surface species provides basic insight into the details of species surface structure which may be used to assign chemisorption site locations with accuracy in favorable cases. Correlation with other surface measurement techniques is particularly valuable in assigning surface structures.

5. "A Coverage-Induced Tilting of CO Molecules Adsorbed on Ni(110)"

ABSTRACT

By means of the combined use of metastable quenching spectroscopy (MQS), thermal desorption spectrometry (TDS) and electron stimulated desorption ion angular distribution (ESDIAD), evidence has been found for a coverage dependent reversible bonding geometry transition for CO chemisorbed on the Ni(110) surface. Over the temperature range of ~90 - 120 K the CO chemisorption axis tilts from its surface normal orientation below $\theta = 0.75$ CO/Ni to an off-normal direction above that critical coverage.

6. "Metastable Angular Distributions from Electron Stimulated Desorption"

ABSTRACT

We have, for the first time, measured by electron stimulated desorption the angular distribution of electronically excited (metastable) species from CO adsorbed on Ni(110). The angular distribution of metastable desorption is strongly peaked in the normal direction, as is also found for ionic desorption products. This indicates that the metastable is repelled along the direction of the bond being broken. We also observe an asymmetry in the azimuthal angular distribution which is correlated with the substrate crystal structure. The metastable exhibits a maximum in its yield versus coverage.

7. "Conformational Changes in Chemisorbed CO on Ni(110) Due to Molecular Interactions: An ESDIAD Study"

ABSTRACT

The surface bonding geometry of CO chemisorbed at 83 K on the Ni(110) surface was studied as a function of CO coverage using the ESDIAD technique. A study of the O^+ angular distribution from CO indicated that at CO coverages below about 0.75 CO/Ni, a normal orientation of the C-O bond exists. Above this coverage, CO species begin to be tilted approximately 19° away from the normal in a plane perpendicular to the Ni atom rows. The O^+ ion angular distribution evolves from a single normal beam to a split beam during this transformation. The yield of positive ions from chemisorbed CO was studied as a function of electron energy. Since a sharp threshold for O^+ emission occurs at the O(1s) core level energy, measurements above this threshold are particularly effective in observing the conformational transformation. In addition, smaller yields of O^{++} and CO^+ have been characterized as functions of the electron energy. The conformational behavior of CO has been correlated with thermal desorption spectra and LEED behavior for the overlayer. The work was carried out in a new ESDIAD analyzer which acquires digital ion angular distribution data. The new apparatus is able to eliminate a serious soft X-ray background present in all photographic ESDIAD measurements. Coherent accumulation of ESDIAD data and subsequent background subtraction yields excellent signal-to-noise ratios for ion angular distributions, and facilitates quantitative analysis of ion beam orientations.

8. "Enhancement of the ESDIAD Method for Imaging Bond Directionality in Chemisorbed Species"

ABSTRACT

The ESDIAD method for imaging adsorbate bond directions by photographic observation of positive ion angular distributions during electron stimulated desorption suffers from inherent low contrast due to background effects. The use of a digital acquisition system designed to overcome this difficulty in ESDIAD measurement is presented. Measurements on a Ni(110) single crystal substrate show the presence of a significant background signal due to soft x-ray generation by electron impact. By subtraction of the background signal, a significant enhancement of positive ion signal-to-noise ratio is achieved in ESDIAD, converting the ESDIAD method into a high contrast, high resolution surface measurement technique. Quantitative studies of the soft x-ray background have shown it to be linearly dependent on electron current density and electron energy, with no change in angular shape. These properties permit an accurate background subtraction procedure to be employed to significantly enhance the capability of the ESDIAD method.

9. "An Enhanced ESDIAD Method for Imaging Molecular Orientations of Adsorbed Species"

ABSTRACT

A striking improvement has been made in the quality of positive ion angular distribution data obtained in electron-stimulated-desorption ion angular distribution (ESDIAD). The improved method has been used to study configurational changes in chemisorbed CO on Ni(110) which are induced by intermolecular interactions at high coverage. CO molecules adsorbed with normal C-O bond orientations on ridge Ni sites tilt away from the normal by $\pm 19^\circ$ in directions perpendicular to the ridges for CO coverages above 0.75 CO/Ni. Evidence for the C-O tilting has also been studied as a function of electron energy. This has demonstrated that an O(1s) excitation process leads to intense and sharp O⁺ ESDIAD beams. The improved ESDIAD method involves the removal of a soft x-ray background signal which originates from electron impact on the metal surface, and is therefore present in all photographic ESDIAD measurements made to date. The angular distribution of the background effect is independent of electron energy and current density. The resultant "pure ESDIAD" patterns show more quantitative details in high and low signal regions than has been seen before.

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